

RUI (Collaborative Research): Ion and Radical Beam Tailored Oxide, Nitride and Germanide Electronic Film Materials

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- This TxSU collaboration with RUI's at Angelo State U (Sauncy – DMR 0210947) & Tarleton State U (Marble – DMR 0210162) addresses important fundamental materials issues related to zinc oxide (ZnO) wide band-gap electronics – specifically, testing theoretically predicted doping strategies for p-type and magnetic semiconductor behavior.

- Silicide and Germanide materials for ULSI applications were also investigated.

- TxSU's novel Radical Atom Ion Beam Sputtering (RAIBS) materials processing capability was utilized (fig 1).

- We pushed the envelope for obtaining high-quality intrinsic epi-ZnO materials (figs 2-3).

- Using our intrinsic epi-ZnO reference materials, we were able to use high resolution x-ray diffraction (HR-XRD, fig 4) to further the understanding of the defects caused by various ZnO doping strategies. Their understanding and control is vital for identifying purely artifact-driven behavior.



Fig. 1: TxSU RAIBS system

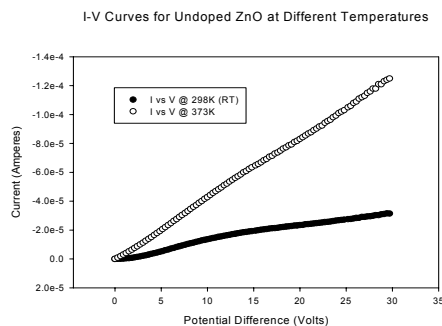


Fig. 3. I-V characteristics of intrinsic ZnO, higher current at elevated T is indicative of intrinsic semiconductor behavior.

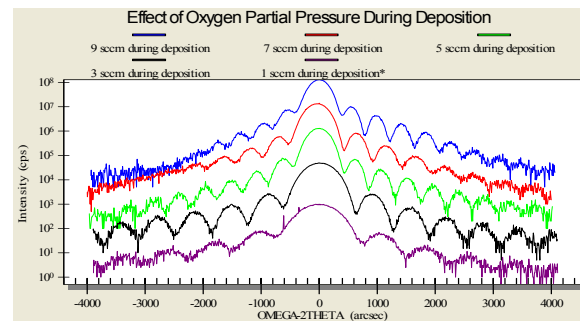


Fig. 2: HR-XRD of epi-ZnO(0002) on sapphire with varying radical oxygen atom exposure.

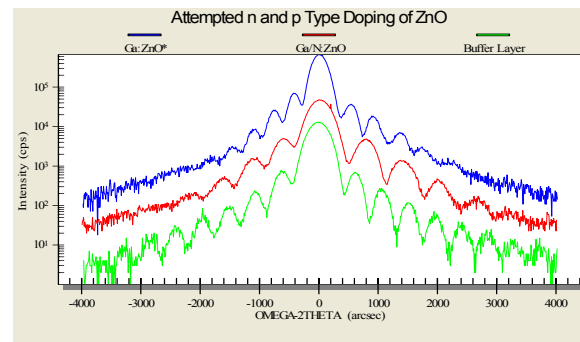


Fig. 4. HR-XRD of intrinsic ZnO versus ZnO on sapphire with Ga and Ga/N doping

Aim of the project:

This RUI project at Texas State University (TxSU) has two main thrusts. The main thrust is the exploration of artificially structured ZnO wide bandgap semiconductor materials. Originally, the thrust was directed towards textured film materials, but the unexpected success of the RAIBS film fabrication process for fabricating single crystalline materials has redirected the effort towards epitaxial materials and extended the scope to include both spintronic (magnetic semiconductor) and opto-electronic film materials. This allows the effort to focus on reduced defect ZnO doped materials that are more useful for testing recent controversial theoretical predictions for possible ZnO p-type doping using nitrogen and Ga-nitrogen co-doping mechanisms. In addition, similar theoretical predictions exist for magnetic ion induced spintronic behavior at room temperature in ZnO. This has met mixed experimental verification, mostly using non-epitaxial doped ZnO systems open to artifacts like magnetic ion clustering. A smaller effort is directed to metastable silicide and SiGe materials of possible interest for ULSI.

Research results:

Sputtering is not ordinarily considered a viable technique for producing high quality compound semiconductor materials. However, we have demonstrated that our unique ability for combining ion beam sputtering (using an oxygen resistant RF ion beam source) with an oxygen atom radical source (RAIBS) is a viable technique for producing high-quality epitaxial ZnO films on sapphire. We are the first US group to seriously investigate this combined RAIBS approach (one other group in Japan is also exploring this technique). To our best knowledge, the narrow high resolution x-ray diffraction (HR-XRD) peak full width half max peak characteristics, low stress states, and pendollosung fringing for our RAIBS fabricated intrinsic ZnO films is unsurpassed even by PLD or MBE/CVD processing. We are using these high quality intrinsic ZnO reference materials as a useful gauge for comparing the defects introduced by proposed Ga and Ga/N co-doping strategies (with and without additional Mn magnetic ions). This will allow us to make a serious experimental study for checking recent theoretical predications for the doped ZnO system by various Japanese and European groups. We are moving towards

the ability to produce interesting doped samples for wide band gap semiconductor and spintronic applications for further analysis by external collaborators (like magneto-optic characterization and magnetic circular dichroism studies) to settle the controversial disagreement whether the ZnO system can produce viable p-type materials or “true” magnetic semiconductors. We have preliminary evidence of weak ferromagnetic behavior at room temperature for our thin (<50 nm) Mn-doped ZnO films, although our attempts to date also indicate that Mn produces significant defects when incorporated into the ZnO matrix. In general, our results indicate that we need to investigate the reduction of defects (and increase film growth rates) in ZnO films by implementing metal alloy versus composite oxide targets possibly combined with RTP type post-annealing. We have observed that Ga doping produces much fewer defects in ZnO resulting in n-type behavior, but that N co-doping strongly adds to the defect structure but also seems to be introducing characteristics suggestive of p-type behavior as suggested by theory. We are working to reduce the defect structure caused by the N doping to reduce artifact characteristics.

In cooperation with Sematech, we have investigated the formation of SiGe layers to produce materials with useful mobility characteristics, and also kinetic mechanisms for prolonging the thermal stability of transition metal mono-silicides. We have successfully tested this approach using CoSi, and are planning to extend this work towards NiSi.

Significance of this work:

We have demonstrated the utility of radical atom processing for zinc oxide and oxynitride film fabrication, an approach that had not been significantly previously investigated. We have made significant progress towards controlling interfacial quality and stress. Heavy Ga doping can still produce epitaxial ZnO materials, but defects are clearly present. The introduction of Mn ions with and w/o N-doping has strong impact on crystalline quality which could provide misleading magnetic artifacts. Processing strategies must be modified to reduce these defects. We have also demonstrated an approach for producing highly stable Co monosilicides on SiO₂ that may be extended to other systems and could prove useful for ULSI gate contacts.

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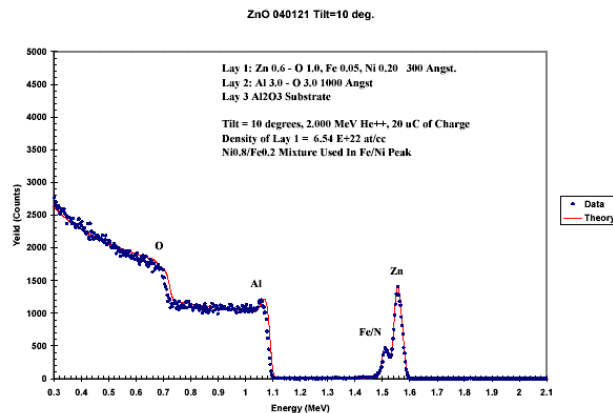


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Education:

This work involves the collaboration of three TxSU MS students (Dana Larison, Casey Smith, Steven Rios), and three TxSU undergraduate students (Isabel Gallardo, Daniel Ralls and Jesse Contreras). During the summer, the PI and graduate students participate in TxSU's HS-LSAMP program. Key interactions with Angelo State U (ASU) and Tarleton State U (TSU) centered around complementary measurements of TxSU film samples by ASU/TSU faculty & undergraduates (example: fig 5). A strong interaction with Sematech was engaged, with TxSU student Larison gaining internship experience.

Fig 5: TxSU Ni doped ZnO film measured by RBS at Tarleton St U



Outreach:

As faculty advisor for the TxSU MAES (Mexican American Engineers and Scientists), the PI helped organize and lead the interactive Spring 2004 "Science Extravaganza" outreach program at TxSU for all 5th & 6th grade public students in San Marcos, TX (fig 6). In addition, Gutierrez served as a member of the American Physical Society Committee on Minorities (COM).



Fig 6: San Marcos 5th and 6th graders engaged in an interactive science/engineering event at the TxSU MAES Science Extravaganza.

This RUI project at Texas State University (TxSU) combines the X-ray Characterization and radical assist ion beam sputtering (RAIBS) film processing capabilities at TxSU with the strong MRI-supported Rutherford Back Scattering (RBS) and optical/electrical characterization capabilities at nearby Tarleton State University (TSU) and Angelo State University ASU -both BS-intensive institutions. The emphasis was towards sharing TxSU film samples for relevant characterization research and integrated education activities at both TSU and ASU. Neither ASU or TSU have in-house film materials processing capabilities. The TSU RBS system is turning out to be a valuable complement to X-ray diffraction and reflectivity for film thickness analysis and interface characterization. In addition, RBS is a useful tool for elemental analysis of layers. ASU capabilities have been augmented by those at Texas Tech U thanks to Sauncy's contact with her former dissertation advisor, Dr Mark Holtz. Holtz has wide bandgap characterization capabilities due to his recent interest with the similar GaN system.

The ULSI front end materials effort has been augmented by a growing interaction with Sematech as originally proposed in the proposal. This is opening up internship possibilities for students like TxSU MS student Dana Larison. Her internship experience has transformed to a permanent full-time process characterization engineer at Sematech. A smaller industry interaction is also present with Agere (Orlando).

Gutierrez has participated in the American Physical Society Committee on Minorities (APS-COM), where he participated in the 2004 APS Minority Scholars selection process, and co-organized the APS COM invited session on "Topics in Nanoscale and Cooperative Phenomena". His group also engaged San Marcos CISD 5th & 6th graders in a hands-on "Science Extravaganza" event at the TxSU campus. The SM-CISD has >50% minority student population. This event is intended to bring students to the TxSU campus, participate in interactive science & engineering projects in actual TxSU science labs, and get students "turned on" to science and engineering related careers. The Science Extravaganza was recognized by a City Proclamation, and has been adopted as a national example by the National Society of Mexican American Engineers and Scientists.